

# Clausius vs. Sackur-Tetrode ideal gas entropy in open systems

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Based on the properties of homogeneous functions of first degree, we derive in a mathematically consistent manner the explicit expressions of the chemical potential  $\mu$  and the Clausius entropy  $S$  for the case of monoatomic ideal gases in open systems within phenomenological thermodynamics. Neither information theoretic nor quantum mechanical statistical concepts are invoked in this derivation. Considering a specific expression/value of the constant term of  $S$ , the derived entropy coincides with the Sackur-Tetrode entropy in the thermodynamic limit. We demonstrate however, that the former limit is not contained in the classical thermodynamic relations, implying that the two aforementioned entropies are distinct in finite systems.

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## I. INTRODUCTION

The first law of thermodynamics presents an expression of the energy conservation principle. In terms of total differentials the former law is given as

$$T dS = dU + P dV - \mu dN, \quad (1)$$

where  $T$ ,  $S$ ,  $U$ ,  $P$  and  $V$  denote the temperature, the (Clausius definition of) entropy, the internal energy, the pressure and the volume, respectively.  $N$  denotes the number of particles and  $\mu$  the chemical potential associated with the particle exchange (for one species of particles). A possible solution of Eq. (1) for the case of monoatomic ideal gases, with respect to the entropy as a function of  $U, V$  and  $N$ , has been initially computed within quantum statistical mechanics, with a Hamiltonian consisting only of kinetic energy contributions, presenting a solution of Boltzmann-Gibbs statistics as well. The obtained result is known as the Sackur-Tetrode (ST) entropy and it has the following expression

$$S_{\text{ST}}(U, V, N) = \lim_{N \rightarrow \infty} k_B \ln \left( \frac{\Phi}{h^{3N} N!} \right) = k_B N \left[ \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln \left( \frac{U}{N} \right) + \frac{5}{2} - \frac{3}{2} \ln \left( \frac{3h^2}{4\pi m} \right) \right], \quad (2)$$

where  $k_B$  and  $h$  are the Boltzmann and Planck constants respectively, and  $\Phi$  is the  $6N$ -dimensional phase-space volume of the region enclosed by the constant energy hyper surface [1]. The term  $m$  denotes the mass of the particles. The factor  $N!$  stems from the traditional way of resolving the Gibbs paradox [2], interpreted by means of the quantum mechanical concept of the particles indistinguishability, taking in this way into account the invariance under permutations. An information theoretical derivation of the ST-entropy has been also demonstrated by A. Ben-Naim in his textbook [3], where the former function is the result of the combination of the following four terms: positional uncertainty, momenta uncertainty, quantum mechanical uncertainty principle and the indistinguishability of the particles. In the same book one may also find an alternative derivation of the factor  $N!$ , with the Schrödinger equation being the point of departure.  $S_{\text{ST}}$  is then expressed in terms of the de Broglie wavelength.

From the mathematical point of view, the ST-entropy in Eq. (2) presents a *homogeneous function of first degree*. We remind that a function  $f : \mathbb{R}_+^q \rightarrow \mathbb{R}$  of class  $C^{m \geq 2}$  is said to be homogeneous of  $\tau$ th degree ( $\tau d$ ) generally, when it satisfies the following relation

$$f(\alpha \mathbf{x}) = \alpha^\tau f(\mathbf{x}), \quad (3)$$

where  $\alpha \in \mathbb{R}_+$  and  $\mathbf{x} \in \mathbb{R}_+^q$ . Then, homogeneity of degree one (1d) is characterized by Eq. (3) for  $\tau = 1$ . Requiring the aforementioned mathematical property as a fundamental property of the thermodynamic entropy  $S$ , we aim in this paper to derive a solution of Eq. (1) for monoatomic ideal gases in open systems within the context of the

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phenomenological thermodynamics. It is demonstrated that the entropy function  $S$  obtained from our homogeneity analysis coincides with the ST-entropy for a properly chosen constant term of  $S$ . In the current derivation however, we do not explicitly invoke the  $N \rightarrow \infty$  limit, in contrast to the  $S_{\text{ST}}$  derivation, as can be seen in Eq. (2). We further show that the first law of thermodynamics does not contain the thermodynamic limit, implying that if 1d-homogeneity is a fundamental entropic property, then the monoatomic ideal gas entropy is not given by  $S_{\text{ST}}$  in Eq. (2) but is given by the Clausius entropy  $S$ . This result is of great theoretical interest, since it indicates that, under the request of the entropic 1d-homogeneity, the statistical background of  $S_{\text{ST}}$  does not succeed to derive the correct entropy expression of monoatomic ideal gases.

The paper is organized as follows. Section II reviews the basic relations characterizing the homogenous functions of first degree. After having outlined the formalism of the former functions, in Section III, we apply it to thermodynamic functions deriving the chemical potential and the entropy expression for monoatomic ideal gases in open systems. Conclusions are presented in Section IV.

## II. HOMOGENEOUS FUNCTIONS OF FIRST DEGREE

Let us consider a 1d-homogeneous (1dH) function  $f : \mathbb{R}_+^q \rightarrow \mathbb{R}$  of class  $C^{n \geq 2}$ . Then, according to Eq. (3) (for  $\tau = 1$ ),  $f(\mathbf{x})$  satisfies the relation

$$f(\alpha \mathbf{x}) = \alpha f(\mathbf{x}). \quad (4)$$

An example of the former function for the case  $q = 2$  can be provided as  $f(x, y) = x \exp(x/y)$ , where  $x_1 = x$  and  $x_2 = y$ . The differentiation of Eq. (4) with respect to  $\alpha$  yields

$$\sum_{i=1}^q x_i \frac{\partial f(\alpha \mathbf{x})}{\partial (\alpha x_i)} = f(\mathbf{x}). \quad (5)$$

Eq. (5) is valid for any  $\alpha \in \mathbb{R}_+$ , thus we can choose  $\alpha = 1$ . We then obtain

$$f(\mathbf{x}) = \sum_{i=1}^q x_i A_i(\mathbf{x}), \quad (6)$$

where  $A_i(\mathbf{x}) := \partial f(\mathbf{x}) / \partial x_i$ . Regarding our example above, we have  $A_1(\mathbf{x}) = A_x(x, y) = (1 + x/y) \exp(x/y)$  and  $A_2(\mathbf{x}) = A_y(x, y) = -\exp(x/y) x^2 / y^2$ . Indeed then,  $f(x, y)$  can be expressed as in Eq. (6), i.e.,  $f(x, y) = x A_x(x, y) + y A_y(x, y)$ . The aforementioned equation is referred to as *Euler's 1d-homogeneous function theorem*, stating that a 1dH-function  $f(\mathbf{x})$  can always be expressed in the form of Eq. (6). It can easily be shown that the relation between Eq. (4) and Eq. (6) is bijective. From the latter equation we see that the functions  $A_i(\mathbf{x})$  are 0d-homogeneous (0dH), i.e.,  $A_i(\alpha \mathbf{x}) = A_i(\mathbf{x})$ , which is verified also from our example,  $A_x(\alpha x, \alpha y) = A_x(x, y)$  and  $A_y(\alpha x, \alpha y) = A_y(x, y)$ . Computing the partial derivative of  $f(\mathbf{x})$  in Eq. (6) with respect to  $x_j$ , we obtain

$$\frac{\partial f(\mathbf{x})}{\partial x_j} = A_j(\mathbf{x}) + \sum_{i=1}^q x_i \frac{\partial A_i(\mathbf{x})}{\partial x_j}, \quad (7)$$

implying

$$\sum_{i=1}^q x_i \frac{\partial A_i(\mathbf{x})}{\partial x_j} = 0. \quad (8)$$

As can be seen, Eq. (8) is satisfied by any 1dH-function and thus it presents another characteristic relation of the former class of functions. In fact, Eq. (8) presents a set of  $q$  conditions, since  $j = 1, \dots, q$ . Due to  $f(x, y)$ , the former conditions take the form

$$x \frac{\partial A_x(x, y)}{\partial x} + y \frac{\partial A_y(x, y)}{\partial x} = x \left( \frac{x}{y^2} + \frac{2}{y} \right) \exp \left( \frac{x}{y} \right) + y \left( -\frac{x^2}{y^3} - \frac{2x}{y^2} \right) \exp \left( \frac{x}{y} \right) = 0, \quad (9)$$

$$x \frac{\partial A_x(x, y)}{\partial y} + y \frac{\partial A_y(x, y)}{\partial y} = x \left( -\frac{x^2}{y^3} - \frac{2x}{y^2} \right) \exp \left( \frac{x}{y} \right) + y \left( \frac{x^3}{y^4} + \frac{2x^2}{y^3} \right) \exp \left( \frac{x}{y} \right) = 0. \quad (10)$$

Now, we want to prove the reverse, namely if Eq. (8) is true, then  $f(\mathbf{x})$  is 1dH. Eq. (8) is valid for any translation  $\tilde{f}(\mathbf{x})$  of  $f(\mathbf{x})$ , i.e.,  $\tilde{f}(\mathbf{x}) = f(\mathbf{x}) + c$ , where  $c$  is a constant, so that  $\tilde{A}_i(\mathbf{x}) := \partial \tilde{f}(\mathbf{x}) / \partial x_i = \partial f(\mathbf{x}) / \partial x_i = A_i(\mathbf{x})$ . Multiplying Eq. (8) by  $dx_j$  and then summing over all  $j$ 's in the aforementioned equation, yields

$$\sum_{j=1}^q \sum_{i=1}^q x_i \frac{\partial \tilde{A}_i(\mathbf{x})}{\partial x_j} dx_j = \sum_{i=1}^q \sum_{j=1}^q x_i \frac{\partial \tilde{A}_i(\mathbf{x})}{\partial x_j} dx_j = \sum_{i=1}^q x_i d\tilde{A}_i(\mathbf{x}) = 0. \quad (11)$$

The change in the order of the summation in Eq. (11) can be performed, since  $\sum_{j=1}^q (\sum_{i=1}^q x_i [\partial \tilde{A}_i(\mathbf{x}) / \partial x_j]) dx_j = 0 < \infty$ . Adding the term  $\sum_{i=1}^q \tilde{A}_i(\mathbf{x}) dx_i$  in Eq. (11), we obtain

$$\begin{aligned} \sum_{i=1}^q \tilde{A}_i(\mathbf{x}) dx_i &= \sum_{i=1}^q \tilde{A}_i(\mathbf{x}) dx_i + \sum_{i=1}^q x_i d\tilde{A}_i(\mathbf{x}) \Rightarrow d\tilde{f}(\mathbf{x}) = d\left(\sum_{i=1}^q x_i \tilde{A}_i(\mathbf{x})\right) \Rightarrow \\ \tilde{f}(\mathbf{x}) &= \sum_{i=1}^q x_i \tilde{A}_i(\mathbf{x}) + a \Rightarrow f(\mathbf{x}) = \sum_{i=1}^q x_i A_i(\mathbf{x}) + (a - c), \end{aligned} \quad (12)$$

where  $a$  is an integration constant. We can always choose  $c = a$ , so that Eq. (12) is identified with Eq. (6). Herewith, we have proven that the conditions in Eq. (8) are necessary and sufficient conditions for having 1d-homogeneity. Thus, they can be considered as an alternative definition of 1dH-functions. An important consequence of Eq. (8) (or equivalently Eq. (11)) is that the differential of the function  $f(\mathbf{x})$  is exact

$$df(\mathbf{x}) = \sum_{i=1}^q A_i(\mathbf{x}) dx_i + \sum_{i=1}^q x_i dA_i(\mathbf{x}) \stackrel{(11)}{=} \sum_{i=1}^q A_i(\mathbf{x}) dx_i = \sum_{i=1}^q \frac{\partial f(\mathbf{x})}{\partial x_i} dx_i, \quad (13)$$

implying simply, that there are indeed functions satisfying Eq. (4).

It is worth remarking that Eq. (8), because of the equality  $\partial A_i(\mathbf{x}) / \partial x_j = \partial A_j(\mathbf{x}) / \partial x_i$  which holds true for any  $C^{n \geq 2}$ -function, can be rewritten as  $\sum_{i=1}^q x_i [\partial A_j(\mathbf{x}) / \partial x_i] = 0$ . One can easily verify that the former equation is the respective result of Eq. (6) for 0dH functions. It becomes obvious then that Eq. (8) fully characterizes both the 1dH-function  $f(\mathbf{x})$  and the 0dH-functions  $A_i(\mathbf{x})$  simultaneously.

### III. MONOATOMIC IDEAL GAS ENTROPY OF THREE INDEPENDENT VARIABLES

We now make use of the results presented in the previous section on 1dH- and 0dH-functions to model thermodynamic quantities. Considering three independent variables, i.e.,  $U$ ,  $V$  and  $N$ , representing the internal energy, the volume and the number of the particles of a system under scrutiny, respectively. Further, we assume a 1dH-function  $S = S(U, V, N)$  as the entropy. Then, according to Eq. (6),  $S$  can be expressed as follows

$$S(U, V, N) = \frac{1}{T(U, V, N)} U + \frac{P(U, V, N)}{T(U, V, N)} V - \frac{\mu(U, V, N)}{T(U, V, N)} N, \quad (14)$$

where

$$\frac{1}{T(U, V, N)} := \frac{\partial S(U, V, N)}{\partial U}, \quad \frac{P(U, V, N)}{T(U, V, N)} := \frac{\partial S(U, V, N)}{\partial V}, \quad \frac{\mu(U, V, N)}{T(U, V, N)} := -\frac{\partial S(U, V, N)}{\partial N}. \quad (15)$$

In thermodynamics, Eq. (14) is referred to as the *Euler equation*. The left hand side of the definitions in Eq. (15) are concrete physical quantities.  $T$ ,  $P$  and  $\mu$  denote the temperature, pressure and chemical potential, respectively. They suppose to be 0dH-functions, otherwise the assumption of  $S$  being 1dH cannot hold true. As shown in the previous section,  $S$  has to satisfy the conditions in Eq. (8). In the thermodynamic notation the former conditions take the form

$$U \frac{\partial}{\partial U} \frac{1}{T} + V \frac{\partial}{\partial U} \frac{P}{T} - N \frac{\partial}{\partial U} \frac{\mu}{T} = 0, \quad (16a)$$

$$U \frac{\partial}{\partial V} \frac{1}{T} + V \frac{\partial}{\partial V} \frac{P}{T} - N \frac{\partial}{\partial V} \frac{\mu}{T} = 0, \quad (16b)$$

$$U \frac{\partial}{\partial N} \frac{1}{T} + V \frac{\partial}{\partial N} \frac{P}{T} - N \frac{\partial}{\partial N} \frac{\mu}{T} = 0. \quad (16c)$$

If the 0dH-functions  $P, T$  and  $\mu$  satisfy Eq. (16), then the differential of  $S$  is exact yielding the first law of thermodynamics, given in Eq. (1). Considering the relations in Eq. (16) simultaneously, they can be written as

$$Ud\left(\frac{1}{T}\right) + Vd\left(\frac{P}{T}\right) - Nd\left(\frac{\mu}{T}\right) = 0. \quad (17)$$

We identify Eq. (17) with the well known *Gibbs-Duhem relation* [4].

Let us now explore the conditions in Eq. (16) for the case of an ideal monoatomic gas in an open system,  $dN \neq 0$ . The expressions of pressure and temperature are given by

$$P(U, V, N) = P(U, V) = \frac{2U}{3V}, \quad T(U, V, N) = T(U, N) = \frac{2U}{3k_B N}. \quad (18)$$

The pressure in Eq. (18) has been derived within the kinetic gas theory. The temperature in Eq. (18), within classical thermodynamics, presents an *ad hoc* definition, being compatible with the equation of state for the ideal gases, i.e.,  $PV = k_B NT$ . Indeed, combining  $P$  and  $T$  in Eq. (18) one obtains the former equation of state. Apparently, the functions  $P$  and  $T$  are 0dH. In the mathematically trivial case of constant pressure and temperature,  $dP = 0 = dT \Rightarrow U \sim N$  and  $V \sim N$ , Eq. (16) yields a constant chemical potential  $\mu$ . In this case, the respective entropy function in Eq. (14) is 1dH and linear with respect to  $N$ , i.e.,  $S(U, V, N) = S(N) \sim N$ . For the general case of varying pressure and temperature i.e.  $dP \neq 0$  and  $dT \neq 0$ , from Eq. (16), we read

$$\frac{\partial}{\partial U}\mu(U, V, N) = \frac{1}{U}\mu(U, V, N) - \frac{1}{N}, \quad (19a)$$

$$\frac{\partial}{\partial V}\mu(U, V, N) = -\frac{2U}{3VN}, \quad (19b)$$

$$\frac{\partial}{\partial N}\mu(U, V, N) = -\frac{1}{N}\mu(U, V, N) + \frac{5U}{3N^2}, \quad (19c)$$

respectively. Solving this system of differential equations, we are able to determine the expression of the chemical potential compatible with Eqs. (1) and (18). The aforementioned system can be solved stepwise. We first solve Eq. (19a). The result will depend on an integration constant  $Z(V, N)$ , with respect to  $U$ . Then, plugging the former result into Eq. (19b),  $Z(V, N)$  reduces to an integration constant  $Z'(N)$ . Finally, following the same procedure with Eq. (19c),  $Z'(N)$  reduces to a constant, which cannot be further reduced. Thus, for varying pressure and temperature, the monoatomic ideal gas chemical potential is determined apart from a constant  $\xi$ , having the expression

$$\mu(U, V, N) = \frac{U}{N} \left[ \xi + \ln\left(\frac{N}{U}\right) + \frac{2}{3} \ln\left(\frac{N}{V}\right) \right]. \quad (20)$$

As expected, the  $\mu$ -function is 0dH. The respective entropy function  $S$  in Eq. (14) is then 1dH, given as

$$S(U, V, N) = k_B N \left[ \ln\left(\frac{V}{N}\right) + \frac{3}{2} \ln\left(\frac{U}{N}\right) + \frac{5}{2} - \frac{3}{2}\xi \right]. \quad (21)$$

Studying the validity of  $S$ , we observe that the function  $S$  in Eq. (21) can be derived by means of the 1d-homogeneity formalism when  $P, T, \mu \neq \{0, const., \pm\infty\}$ , beforehand, and when  $dU \neq 0$ ,  $dV \neq 0$  and  $dN \neq 0$ , simultaneously. If one of the former differentials is equal to zero, implying that the respective variable is a constant, then the 1d-homogeneity formalism is not applicable, since in this case not all of the partial derivatives of  $S$ , i.e.,  $1/T$ ,  $P/T$  or  $\mu/T$  are 0dH.

Comparing now the Clausius ideal gas entropy  $S$  in Eq. (21) with the Sackur-Tetrode entropy  $S_{ST}$  in Eq. (2), we observe that they both have the same form when  $\xi$  takes the value  $\xi = \ln\left(\frac{3h^2}{4\pi m}\right)$ . This specific expression of  $\xi$  cannot be obtained by virtue of the 1d-homogeneity analysis but only within quantum statistical mechanics. However, even then, it is merely a constant and has no physical impact on the entropy expression. So, we observe that the physical part of Sackur-Tetrode entropy coincides with the one of the ideal gas entropy  $S$  in the  $N \rightarrow \infty$  limit. We stress that the analytical expression of ST-entropy is obtained after the explicit computation of the former limit, as can be seen in Eq. (2), while  $S$  has been derived in practice for any  $N > 0$ . Thus, the two aforementioned entropies may be identified only under the assumption that the thermodynamic limit is implicitly included in the thermodynamic relations. This in turn would imply taking into account the restrictions mentioned above regarding the 0dH-functions  $T, P$  and  $\mu$ , that as much the energy  $U$  as the volume  $V$  are considered in the same limit. If this is the case, then one has to be very careful in discussing phenomenological thermodynamics of finite systems. In different case, studying ideal gases in open systems for finite  $N$  we have  $S \neq S_{ST}$ , yielding merely the same picture in the  $N \rightarrow \infty$  limit.

A possible way to shed light on the aforementioned issue, namely whether phenomenological thermodynamics implicitly contains the thermodynamic limit, or equivalently whether  $S$  and  $S_{\text{ST}}$  are identical, is by considering the general solution (gs) of the differential FLT in Eq. (1), regarding the ideal gas entropy function. The latter is given as in Eq. (21), with the  $\xi$ -term being a function of  $N$ , i.e.,  $\xi \rightarrow \Theta(N)$ , namely

$$S_{\text{gs}}(U, V, N) = k_{\text{B}}N \left[ \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln \left( \frac{U}{N} \right) + \frac{5}{2} - \frac{3}{2} \Theta(N) \right]. \quad (22)$$

In this general case, the chemical potential,  $\mu_{\text{gs}} = -T(\partial S_{\text{gs}}/\partial N)$ , may generally not preserve the 0dH property. From Eqs. (2) and (22), we observe that in the case of ST-entropy the  $\Theta$ -function in finite systems is inhomogeneous and has the explicit expression

$$\Theta_{\text{ST}}(N) = \xi + \frac{2}{3} \left[ 1 - \ln(N) + \frac{\ln(N!)}{N} \right], \quad (23)$$

satisfying the  $\lim_{N \rightarrow \infty} \Theta_{\text{ST}}(N) = \xi$  limit. Let us then explore which is the most general expression of  $\Theta(N)$  being compatible with 1d-homogeneity,  $S_{\text{gs}} \rightarrow S_{\text{gs}}^{\text{1dH}}$  (and  $\mu_{\text{gs}} \rightarrow \mu_{\text{gs}}^{\text{0dH}}$ ). Therefore, we compute again the conditions in Eq. (16), in terms of  $S_{\text{gs}}$  now. From the first two conditions we do not obtain any new information, yet the last one yields

$$N \frac{\partial^2 \Theta(N)}{\partial N^2} + 2 \frac{\partial \Theta(N)}{\partial N} = 0 \quad \Rightarrow \quad \Theta(N) = a_1 - \frac{a_2}{N}, \quad (24)$$

where  $a_1$  and  $a_2$  are integration constants. Plugging the result in Eq. (24) into Eq. (22) we obtain

$$\begin{aligned} S_{\text{gs}}^{\text{1dH}}(U, V, N) &= \frac{1}{T(U, V, N)}U + \frac{P(U, V, N)}{T(U, V, N)}V - \frac{\mu_{\text{gs}}^{\text{0dH}}(U, V, N)}{T(U, V, N)}N + \frac{3}{2}k_{\text{B}}a_2 \\ &= k_{\text{B}}N \left[ \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln \left( \frac{U}{N} \right) + \frac{5}{2} - \frac{3}{2}a_1 \right] + \frac{3}{2}k_{\text{B}}a_2, \end{aligned} \quad (25)$$

where  $\mu_{\text{gs}}^{\text{0dH}} = \mu$  in Eq. (20) with  $a_1 \equiv \xi$ . Comparing Eqs. (21) and (25), it becomes obvious that  $S_{\text{gs}}^{\text{1dH}}$  contains an extra additive constant. However, in Eq. (12) we showed that such a constant can always be transformed away. Thus, the  $\frac{3}{2}k_{\text{B}}a_2$ -term has neither physical nor mathematical impact on  $S_{\text{gs}}^{\text{1dH}}$  so that the former is identified with  $S$  in Eq. (21). Eq. (24) then, unveils that the thermodynamic limit is *not* included in the phenomenological thermodynamic equations. If it would be included, then the  $a_2$ -term would not appear,  $\lim_{N \rightarrow \infty} a_2/N = 0$ . Accordingly, the Clausius 1dH entropy function  $S$  in Eq. (21), derived by means of purely thermodynamic relations, is distinct from the 1dH ST-entropy, derived within statistical mechanics in Eq. (2).

#### IV. CONCLUSIONS

Studying homogenous functions of first degree (1d), we demonstrated that they can be defined through a set of  $q$ -specific conditions given in Eq. (8), where  $q$  denotes the number of independent variables of the aforementioned functions. If the 1d-homogeneous function under consideration is the thermodynamic entropy, then the former conditions, expressed compactly in a single equation, are identified with the well-known Gibbs-Duhem relation.

Considering particularly the pressure  $P$  and the temperature  $T$  for the case of monoatomic ideal gases in open systems, where the number of particles  $N$ , the internal energy  $U$  and the volume  $V$  are the independent variables, we derived by means of the 1d-homogeneity conditions, the analytical formulas of the associated chemical potential  $\mu$ , related to the particle exchange, and the associated thermodynamical entropy  $S$ . Interestingly enough, for  $dP \neq 0$  and  $dT \neq 0$  ( $\Rightarrow d\mu \neq 0$ ), the former entropy coincides with the well known Sackur-Tetrode entropy  $S_{\text{ST}}$ , apart from a non-physical  $N$ -translation. In practice however, distinct physical conditions are required for their derivation. In fact, the two aforementioned entropies can be identified to each other only under the assumption of a “hidden” thermodynamic limit in the phenomenological thermodynamic relations. We explicitly showed yet, that the former assumption does not hold true. Accordingly, the Clausius entropy  $S$ , derived on the ground of homogeneous functions of degree one within phenomenological thermodynamics differs from the Sackur-Tetrode entropy  $S_{\text{ST}}$ , derived within statistical mechanics, sharing merely the same expressions in the thermodynamic limit.

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